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THERMAL DECOMPOSITION OF TNT (U)

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THERMAL DECOMPOSITION OF TNT (U)

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THERMAL DECOMPOSITION OF TNT

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ABSTRACT: Partially decomposed TNT has been obtained by heating samples at 200°C for periods of approximately sixteen hours. Seven pure compounds have been isolated from the decomposition residue by chromatographic procedures. Three of these have been identified as 2,4,6-trinitrobenzaldehyde, 2,4,6-trinitrobenzyl alcohol and 4,6-dinitroanthranil. Analyses of the unidentified compounds indicate that they may be oxidation-reduction products of TNT.

Although the mechanism of the decomposition process has not been established, the products isolated support the theory that it proceeds through an oxidative attack at the methyl group by nitro groups in the compound. Some generalizations are made regarding the thermal stabilities of polynitro aromatic compounds having oxidizable substituents. Also, predictions are made as to substituents that would raise the melting point of the trinitrobenzene molecule without marked reductions in its thermal stability.

CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, SILVER SPRING, MARYLAND

NAVORD Report 6831 1 May 1960

This report covers the progress made in a study of the thermal decomposition of TNT. The objective of this project is to shed additional light on the mechanisms by which this and other high energy compounds decompose at elevated temperatures and thereby provide useful information for the design and synthesis of heat resistant high explosive compounds. This work was performed under Task No. FR-44, Chemistry of High Energy Compounds, and Task No. 301-664/43006, Explosives Applied Research.

W. D. COLEMAN
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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INTRODUCTION

The development of high velocity vehicles for the delivery of warheads has introduced the problem of aerodynamic heating to explosives technology. This is especially true with conventional high explosives, many of which decompose when heated to temperatures above their melting points. Most conventional explosives when subjected to the temperatures encountered at or near the surfaces of manned supersonic aircraft or of missiles during reentry into the earth's atmosphere might either explode prematurely or be rendered ineffective by excessive decomposition.

A considerable effort has been expended in the investigation of the thermal stability of high explosives, the greater portion of this work being directed toward the study of the kinetics of the decomposition processes. A better understanding of the mechanisms of these processes would greatly enhance the organic chemist's chances of designing and synthesizing explosive compounds having greater heat resisting capabilities. To help elucidate these mechanisms, the isolation and identification of the intermediate products of controlled decompositions seemed worthwhile. The investigation herein reported has been performed with this as the objective, and 2,4,6-trinitrotoluene (TNT) has been chosen for the initial study. The work is still in progress and this is intended only as a progress report.

REVIEW OF THE LITERATURE

It has long been known that when TNT is subjected to the conditions of the vacuum stability test it gives off relatively small quantities of gaseous products. Above 200°C, however, it apparently undergoes extensive decomposition, the products of which remain in the molten solution. Farmer (1) found that at 135-140°C, TNT yields 1cc of gas per gram in 100 hours, whereas 1,3,5-trinitrobenzene and picric acid required temperatures of 190-195°C and 150-155°C, respectively, for the evolution of comparable amounts of gas in the same length of time. The temperature required for tetryl was 115-120°C, considerably below that of TNT.

R. Robertson (2) found that after 40 hours at 140°C, 1 kg of TNT evolved gas at the rate of 9 cc per hour. He concluded that a very complex mixture of reaction products resulted, one of which resembled the product of the reaction of TNT with alkali and sunlight.

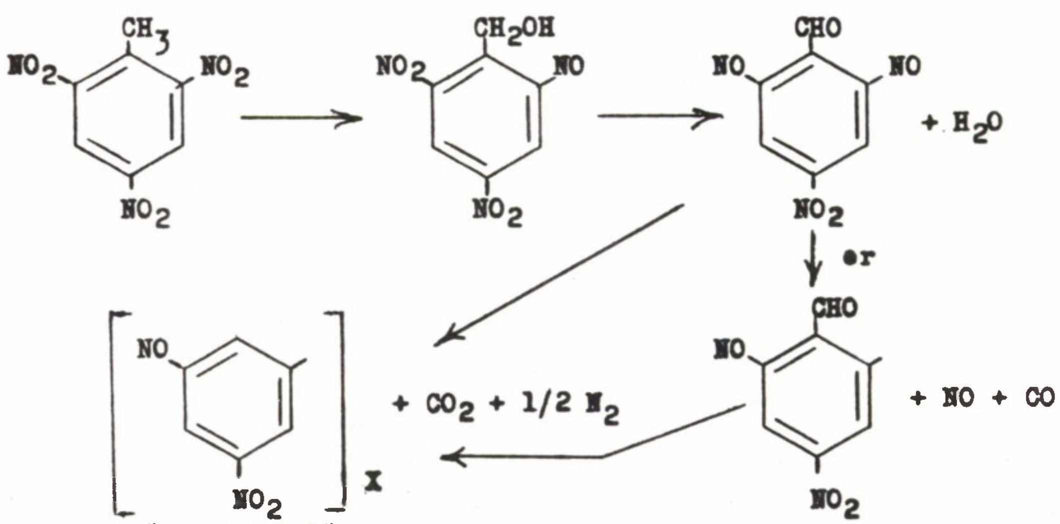
The kinetics of the thermal decomposition of TNT have been reported by A. J. B. Robertson (3,4), Wiseman (5,6), and Edwards (7,8). In these studies, the decompositions were performed in closed reaction vessels and reaction velocities were followed by changes in pressure. There is general agreement that at higher temperatures the reaction takes place in the vapor phase and is apparently first order. At lower temperatures the decomposition is predominantly a much more complex autocatalytic liquid phase reaction. After an initial pressure increase, probably due to vaporization, there is generally an accelerating reaction which terminates in ignition. The length of the quiescent period depends upon the temperature and is practically nil at temperatures in excess of about 300°C. The color of the sample changes to dark brown then to almost black during the latter stages of the accelerated reaction. Wiseman also found that at 200°C the initial reaction in molten TNT involves the production of a high melting substance which lowers the setting point of the sample. It was further noted that this reaction occurs without the evolution of any appreciable quantity of gas. A. J. B. Robertson used atmospheres of air, nitrogen and hydrogen and found that changing from one to the other did not change his results. He also reported that illumination with ultraviolet light prior to heating reduced the quiescent period, but that the total induction period prior to ignition was not changed. This was attributed to a reduction in the acceleration constant and a greater degree of decomposition prior to ignition.

Edwards studied the decomposition in the temperature range 280-450°C and reported no appreciable differences between the thermal reactions of grade I, and pure alpha, beta, and gamma TNTs. Working with mixed samples, he also found that the addition of 1% 2,2',4,4'-tetranitrostilbene or 1% "white compound" (1,9-dicarboxy-2,4,6,8-tetranitrophenazine 10-oxide) reduced the thermal stability, the latter having the greater effect. The addition of 1% 2,4,6-trinitrobenzoic acid or 2,2',6,6'-tetranitroazoxytoluene, on the other hand, had no visible effect. It was also reported that although the length of the induction period was only slightly shorter in hard glass than in quartz, it was greatly reduced in soda glass.

Adams, Rowland and Wiseman (9) found that at the end of the catalytic period approximately one atom of carbon, one atom of nitrogen, two atoms of oxygen and one molecule of water had been eliminated as gaseous products. Nitric oxide, carbon monoxide and carbon dioxide as well as water and nitrogen were found among the products. Most of the nitric oxide and carbon monoxide were produced early in the decomposition process, and the nitric oxide content decreased on prolonged heating.

These authors decomposed α-TNT in air and extracted the residue with toluene. A brown toluene-insoluble fraction was isolated which did not melt below 300°C, was appreciably soluble in TNT at 80°C and was a strong decomposition catalyst. The elemental analysis (C, 44.6; H, 1.85; N, 17.1) corresponded to the imperical formula $C_6H_3N_2O_{3.75}$. The toluene soluble fraction contained, along with the unchanged TNT, a yellow substance which they called "Compound A". This substance possessed the peculiar characteristic of imparting a red stain to most surfaces with which it came in contact. Evidence indicated that it contained one benzene ring, and Robertson (10) later showed it to be an even better decomposition catalyst than the toluene-insoluble fraction. Chemical examination showed that the soluble fraction neither formed a dinitrophenylhydrazone nor did it react rapidly with bromine in carbon tetrachloride. It did, however, rapidly decolorize solutions of potassium permanganate in cold acetic acid.

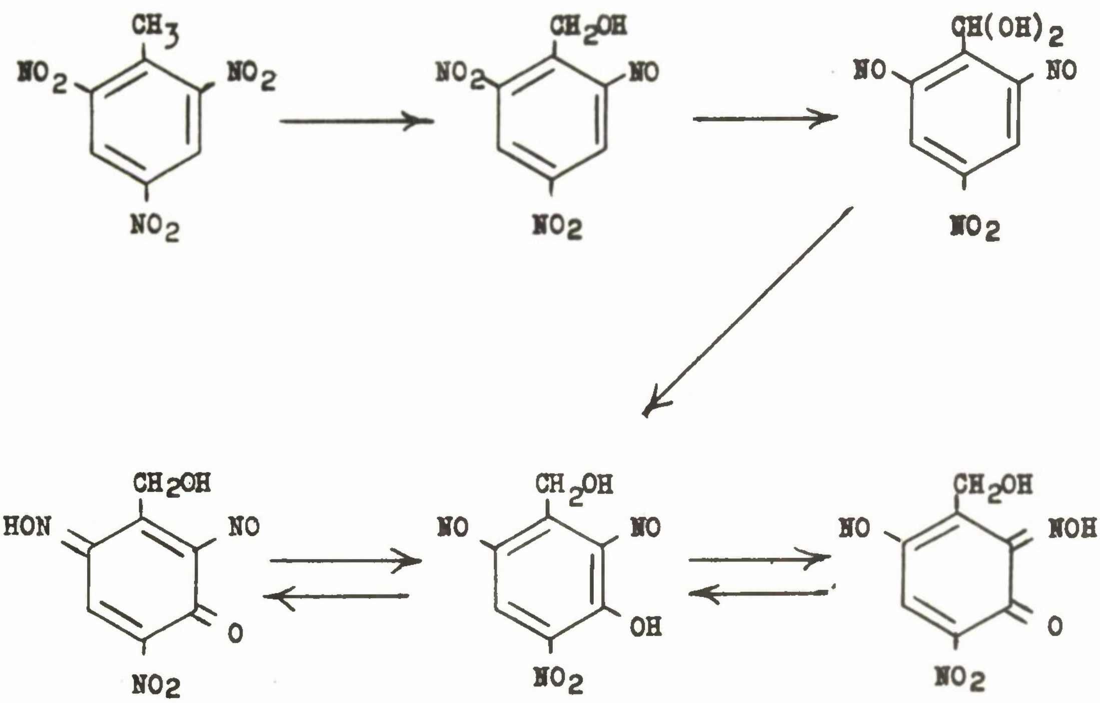
The authors proposed the following sequence of reactions as a possible route for the decomposition.



"Compound B"

It was pointed out that the high melting point and brown color of "compound B" suggested that it was an azo compound.

The findings of Bamberger (11) and Schultz and Ganguly (12) were offered in support of the above sequence of reactions. Bamberger found that the irradiation of *o*-nitrobenzyl alcohol gave *o*-nitrobenzaldehyde, *o*-nitrosobenzaldehyde, and anthranil. The formation of *o*-nitrobenzoic acid and indazolylbenzoic acid was suspected. Schultz and Ganguly isolated a 0.8% yield of a mixture of 4-nitro-2-nitroso-1-hydroxymethyl-5,6-benzoquinone 6-oxime (A) and the 3,6-benzoquinone isomer (B) by the photomerization of TNT. The following sequence of transformations was offered to explain the formation of these compounds.



B A

These results were offered as evidence of an intramolecular oxidation-reduction reaction in the photochemical decomposition of TNT. However, when it is considered that the products isolated after two years of irradiation represented only a small fraction of the starting material, it is obvious that appreciable amounts of other decomposition products were present. The fact that the route for the formation of the quinone oximes was assigned without isolating any of the other reaction products places the assignment in the realm of speculation. Moreover, the formation of a dihydroxymethyl intermediate followed by the migration of an hydroxyl to the ring seems questionable on the basis of the known reactions of compounds of this type. The results of Schultz and Ganguly are not in complete agreement with those of Bamberger.

Summaries of the work on the thermal decomposition of TNT and other high explosives are given by Ubbelohde (13) and Wiseman (14).

RESULTS

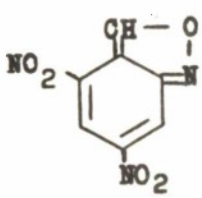
In the current investigation, recrystallized Grade I TNT was decomposed in air at 200°C and atmospheric pressure by heating batches of approximately 15 g in Pyrex test tubes capped by loosely fitting glass stoppers in a vacuum stability block. This arrangement limited the circulation of air in the atmosphere above the sample but permitted the escape of evolved gases. Losses due to sublimation were negligible. Samples were placed in the block at 200°C and held at this temperature for 16 hours, after which, in order to remove the samples, it was necessary to allow the block to cool to temperatures at which it was considered safe to handle the decomposition mixtures. Allowing the block to cool to approximately 80°C required an additional four to five hours.
In several of the decompositions, ignition of the samples occurred before the end of the 16-hour period and was probably due to inadequate temperature control. The temperature was regulated during the earlier experiments by a bimetallic thermoregulator operating several degrees above its intended range and it is likely that control was poor. In later runs, a Brown Instrument Company recorded-controller capable of controlling the temperature at 200°C to within 1°C was used. There were no ignitions and the extent of decomposition was considerably less than in the earlier experiments. The samples were heated during overnight periods and were unattended.

It appeared that in this temperature range slight variations greatly affected both the induction period and the extent of decomposition. Samples heated at 150°C and 180°C for 70 hours showed only slight decomposition indicated by melting point depressions of 1°C and 3°C, respectively. The latter sample was light brown on solidification. Several samples ignited after 37 to 39 hours at 200°C whereas at 210°C, the time required for the ignition of three samples was 14 to 16 hours.

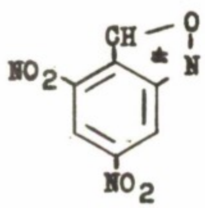
Although the nature of this work precludes a quantitative treatment, especially in its early stages, estimates of the extent of decomposition have been made. This varied between 10 and 25%, the uncertainty being partially attributable to temperature variation. In all cases the products were dark brown crystalline solids, the setting points of which were not determined.

Initial small scale chromatographic studies of the decomposed material indicated the presence of a large number of discrete chemical compounds. The first step in the attempted resolution of this complex mixture was an extraction with boiling benzene. Most of the material dissolved, leaving a brown powder which did not melt below 300°C and burned with intumescence when ignited by a flame. A brown partially crystalline product remained after evaporation of the benzene. These fractions were very similar to the toluene-soluble and insoluble fractions of Adams, Rowland and Wiseman (9). Exploratory chromatography indicated that the insoluble fraction was not a single compound but a mixture containing several components. No effort has as yet been made to resolve this mixture.

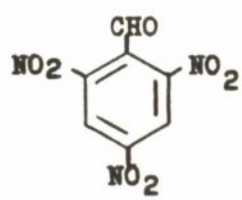
In the initial attempt to isolate pure compounds from the benzene-soluble fraction, TNT, 4,6-dinitroanthranil (I), 2,4,6-trinitrobenzaldehyde (II) and a very small quantity of an amber colored crystalline compound (III) were obtained. Compounds I and II were identified by elemental analyses



I



Ia

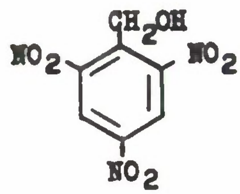


II

and mixed melting points with authentic samples[a].

A single elemental analysis of the unidentified compound III, 217-8°C, indicates that it is a reduction product and, except for the high nitrogen, the analysis fits the empirical formula $C_7H_6N_3O_4$ reasonably well. It might conceivably be one of the tetranitrohydrazotoluenes.

Subsequent attempts to resolve the soluble fraction chromatographically resulted in the isolation of 2,4,6-trinitrobenzyl alcohol (V)



V

and unidentified compounds IV (m.p. 225 - 7°C), VI (m.p. 132 - 4°C) and VII (m.p. 221 - 2°C). Elemental analyses of IV and VII indicate that these compounds, like III, are probably reduction products of TNT. Compound VI is probably an oxidation product.

The amounts of the several products isolated varied considerably from run to run, but the ranges are estimated to be as shown in Table 1. It should be understood that these estimates are based on far from perfect separation techniques and may be considerably on the low side.

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[a] The authentic sample of I was prepared according to the method of Splitter and Calvin (15) who made it by the titanous chloride reduction of II and represented its structure as Ia. In view of the behavior of this compound on chromatographic columns, it is very unlikely that such a charged configuration contributes appreciably to its true structure. In the chromatographic procedures employed in this work, I has been found to follow TNT and to precede II on the columns. The molecular size of these compounds being about equal, the relative polarizabilities of the three compounds on columns of polar adsorbents are probably in the same order as their positions on the columns. A structure such as Ia would probably be far more polar than either of the other two compounds and would behave quite differently on a chromatographic column. It is very probable that the true structure is more correctly represented by I.

Table I

Thermal Decomposition of TNT

16 Hours at 200°C

Products	Weight %
Unreacted TNT	75 - 90
4,6-Dinitroanthranil	2 - 4
2,4,6-Trinitrobenzaldehyde	1 - 2
2,4,6-Trinitrobenzyl alcohol	0.1 - 0.2
Compound III, m.p. 217-8°C	ca. 0.1
Compound IV, m.p. 225-7°C	0.1 - 0.2
Compound VI, m.p. 132-4°C	ca. 0.04
Compound VII, m.p. 221-2°C	ca. 0.1
Benzene-insoluble fraction	0 - 13

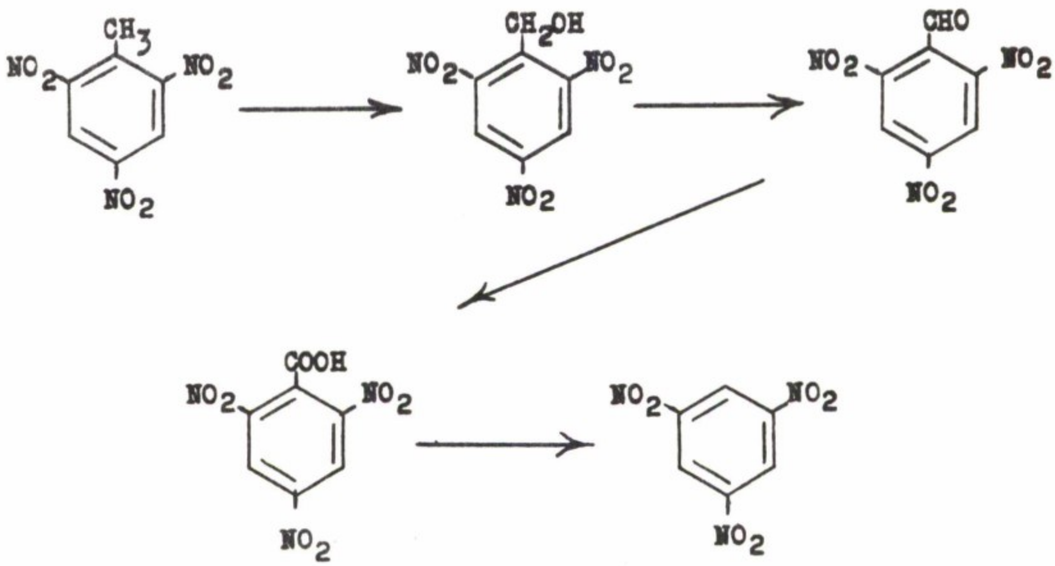
DISCUSSION OF RESULTS

The isolation of II and V from the decomposition residue suggests that at 200°C, the decomposition takes place through oxidative attack at the methyl group. Such an attack might be due either to air oxidation or to the interaction of the methyl group with the nitro groups present in the compound. The former possibility has been substantially ruled out by Robertson's (4) finding that the thermal reaction does not vary appreciably when performed in atmospheres of air, nitrogen and hydrogen. In exploratory decompositions carried out during the course of this research, changing from atmospheres of air to atmospheres of nitrogen did not appreciably change the induction period.

The comparison of the results of the photochemical decomposition of TNT and related compounds with the results of thermal decomposition of TNT seems to be valid. However, the use of these results as concrete evidence of the similarity of the two processes should be avoided until further proof is obtained. Although the evidence favoring intramolecular reaction in photochemical decomposition is strong, the mechanism in thermal decomposition may be quite different. Under conditions where TNT is held in a molten state at

elevated temperatures, the close approach of the substituents on adjacent molecules may cause intermolecular interaction to predominate. The presence of II and V among the products apparently indicates that the reaction is at least partially intermolecular, but the possibility that I may very well be an intramolecular oxidation-reduction product is not ruled out. To accept these products as evidence for either mechanism would not be valid at this stage of the investigation.

If II and V are oxidation products, it might be expected that the reaction would go a step further and form 2,4,6-trinitrobenzoic acid. Since this acid decarboxylates readily at elevated temperatures, one would expect 1,3,5-trinitrobenzene (TNB) as the eventual product.



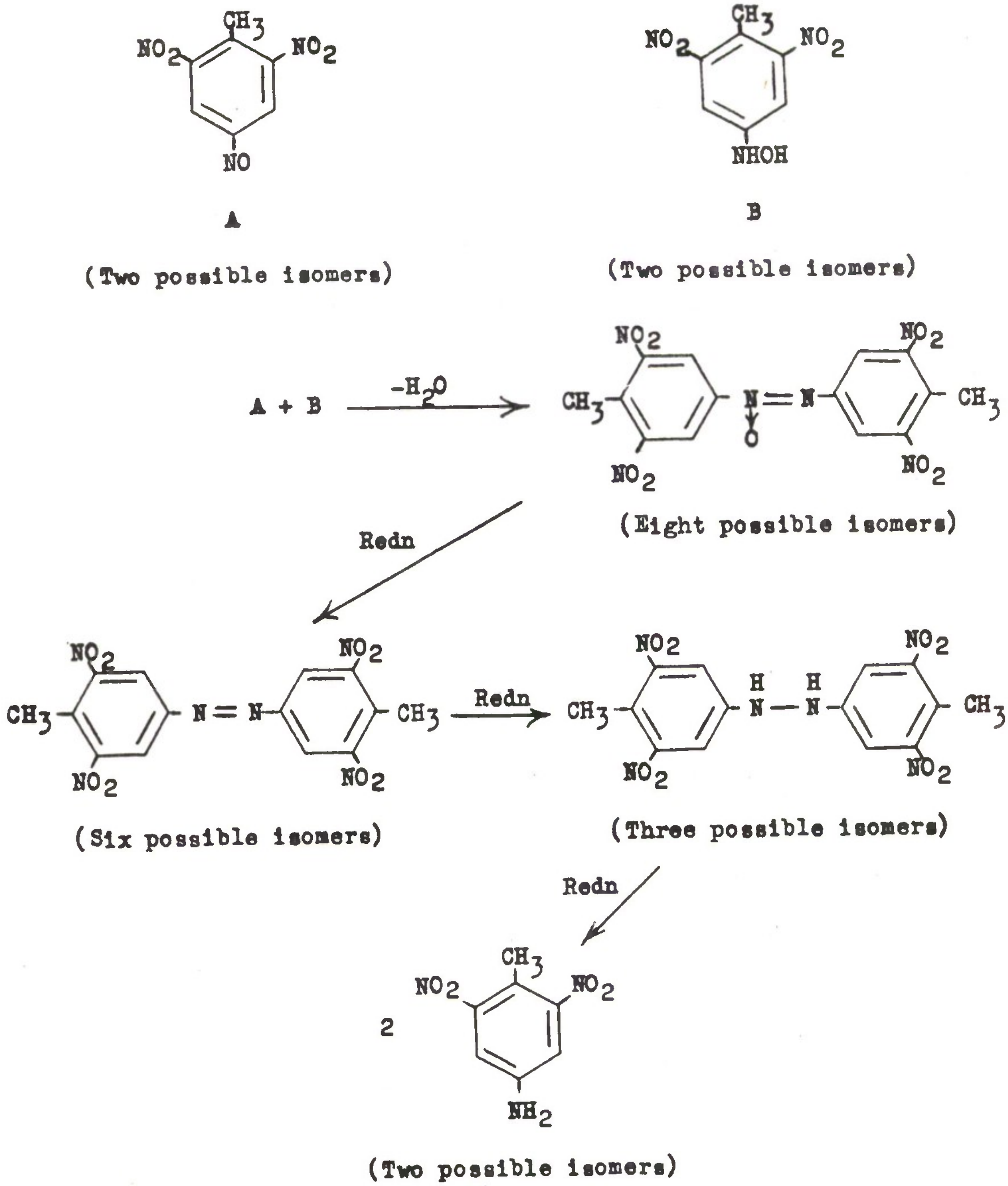
Exploratory chromatography showed that mixtures of TNT, TNB and I were readily separated on silicic acid-Celite columns when developed with benzene-*n*-hexane. The TNB appeared as a zone between the other two components on the columns.
A careful chromatographic search of the decomposition residue in the region TNT - 2,4,6-trinitrobenzaldehyde indicated that TNB was not present. This leads one to conclude that either the aldehyde is stable under the conditions of the decomposition or that it reacts further to form products other than 2,4,6-trinitrobenzoic acid. The latter conclusion seems to be the more valid. Samples of II (4 g), II plus dinitromesitylene (2 g each) and II plus *p*-nitrotoluene (2 g each)

all ignited in less than thirty minutes when heated at 200°C. It seems extremely unlikely therefore that II is stable under the conditions of the decomposition. However the low concentrations in which the compound is found may account for a retardation in the rate of its further reaction. It is not unreasonable that II may have accumulated during the cooling off period of four to five hours.

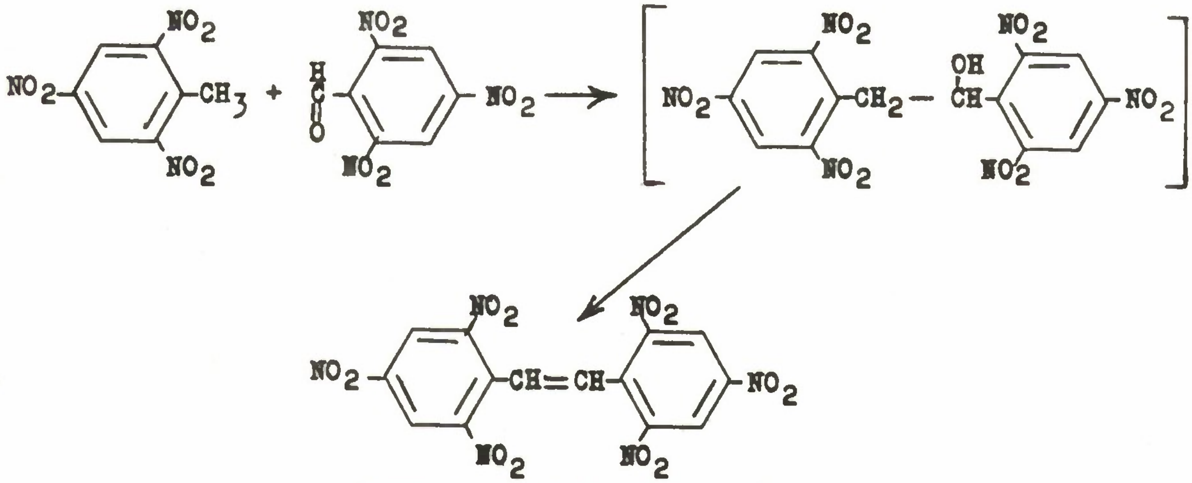
This work has not progressed to the point where a mechanism for the formation of I can be offered. However, several findings may be of value in future determinations of the route by which this compound is produced. It will be observed that I contains the elements of TNT minus one molecule of water. The question then arises, is this compound produced by the direct dehydration of TNT? To check this possibility, TNT was mixed with a slight molar excess of phosphorus pentoxide and heated at 140°-160°C for eighteen hours. On extracting the mixture with benzene and evaporating the solution to dryness, the TNT was recovered almost quantitatively. It was almost white and melted at 81-81.5°C without recrystallization.

Splitter and Calvin (15) prepared I by the titanous chloride reduction of II. Since the aldehyde is a product of the decomposition reaction, and since it is apparently not oxidized to the corresponding acid, it seems plausible that it is a precursor to I. The reducing agent or agents may be found among the other products of the reaction.

If the reaction which produces II and V as oxidation products also produces such compounds as nitrosodinitrotoluene (A) and dinitrotolylhydroxyl amine (B) as reduction products, these may interact to form a number of additional compounds.

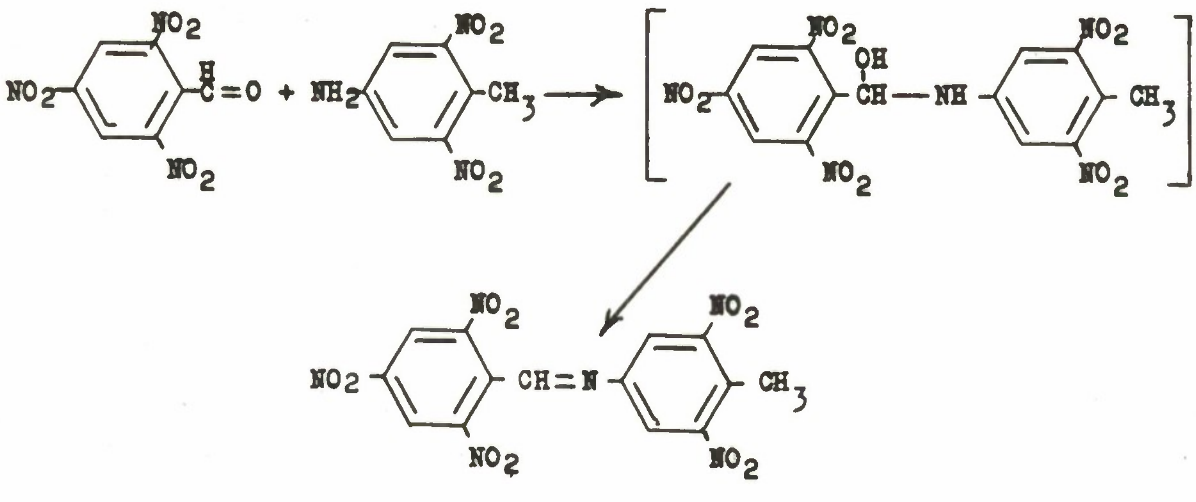

A
(Two possible isomers)
B
(Two possible isomers)
A + B
$-H_2O$
(Eight possible isomers)
Redn
(Six possible isomers)
Redn
(Three possible isomers)
Redn
2
(Two possible isomers)

Decomposition may also occur by the interaction of the methyl group of TNT with the carbonyl of II. Under normal conditions the carbonyl of the aldehyde does not react with active methyl or methylene groups. Under the drastic conditions encountered during the decomposition, however, such a reaction might conceivably occur with the formation of 2,2',4,4',6,6'-hexanitrostilbene.



(Two Possible Isomers)

The dinitrotoluidines may also react with II to form Schiff bases.



(Four Possible Isomers)

When the number of possible isomers, both structural and geometric, that may be produced in these reactions is considered, the complex nature of the decomposition residue is understandable. If we add to these the multimolecular products which may result from the reaction of more than one center in the same molecule, the possibilities become staggering.

During this investigation it became apparent that polynitro aromatic compounds having substituents susceptible to oxidation by the nitro groups would not be suitable for high temperature applications. This premise was supported by the works of Blais, Warman, Siele, and Matsuguma (16,17) who tested TNB and sixteen of its derivatives for high temperature application. Of these, only TNB, DATB, TATB and 2,4,6-trinitroaniline were thought to be worthy of further consideration. TNB was found to be stable at temperatures up to 300°C, but its low melting point makes it undesirable for applications above 120°C. The introduction of amine groups made the compounds somewhat less stable than TNB but raised the melting points to such an extent as to make them more suitable for use at high temperatures. This is particularly true of DATB and TATB.

Since the TNB molecule is thermally stable at temperatures far above its melting point, it appeared that the substitution of non-oxidizable substituents for its hydrogens might produce stable high melting structures. An ideal substituent would seem to be the 2,4,6-trinitrophenyl group itself. Such substitutions would produce 2,2',4,4',6,6'-hexanitrobiphenyl, 2,2',2",4,4',4",6,6',6"-nonanitroterphenyl and 2,2',2",2"',4,4',4",4"',6,6',6"'-dodecanitrotetraphenyl. The latter two compounds would probably be difficult to make and the crowding in the molecules might detract from their stabilities. However, 2,2',4,4',6,6'-hexanitrobiphenyl seems to offer possibilities. This compound has been used in explosive applications (18) but no record of its use as a heat resistant explosive could be found.

CHROMATOGRAPHY

In the initial attempt to resolve the benzene-soluble fraction of the decomposition residue, it was chromatographed on columns of silica/b using dilute solutions of methanol in

/b "Silica for Chromatographic Columns", 50-200 mesh, manufactured by the G. Frederick Smith Chemical Company, Columbus, Ohio.

benzene as developers. Zones were located by extruding the developed chromatograms from the tubes and streaking with saturated solutions of potassium hydroxide in methanol. Representative chromatograms are shown in Figures 1, 2, and 3. These representations, particularly Figure 2, are somewhat idealized as the variations in the rates of movement in different parts of the columns made the chromatograms considerably more irregular than is indicated. Figure 1 represents five columns, all of which were very similar, each having been loaded with approximately 7 g of the benzene-soluble fraction. A total weight of 37 g of material was chromatographed. The combined effluents contained 30 g of solids leaving 7 g in combined zones 1, 2, and 3.

Rechromatographing the solids recovered from the combined initial effluents on six columns of silica resulted in chromatograms represented by Figure 2. Solids in the amount of 28 g were recovered from the effluents from these columns leaving 2 g of material distributed among the various zones on the columns. Each column therefore apparently contained small amounts of a large number of compounds. It was difficult in some cases to distinguish between true zones and variations in intensity within zones. It would be folly to assume that each band on the column contained primarily a single component. Although the streak technique was used, many of the zones were visible without streaking. Rather than attempt to remove each band as a zone, the columns were cut into groups of bands, as indicated, to be rechromatographed later.

Figure 3 represents five chromatograms that resulted from rechromatographing the 28 g of solids recovered from the effluents from the columns represented by Figure 2. The solids recovered from the combined zones 1 and the effluents were primarily TNT and weighed 24 g.

The material in zone 2 was a mixture and attempts to resolve it chromatographically on silica failed. Fractional crystallization eventually yielded small amounts of I and II. Using silicic acid/c - Celite/d 5:1 as the adsorbent and

---

/c Mallinckrodt, Analytical Grade, 100 mesh powder.

/d "Celite 535" manufactured by the Johns-Manville Company.

benzene-n-pentane solutions as developers, a fraction of this material was separated into two zones. The lower zone contained the anthranil and the upper zone the aldehyde.

Several attempts to secure pure compounds from the chromatograms represented by Figure 2 were unsuccessful. No attempts were made to resolve the dark brown tarry materials from the chromatograms represented by Figure 1. However, zone 3 contained a small amount of material that was apparently identical with the benzene-insoluble fraction.

The amount of starting material adsorbed on each column during this separation would ordinarily be considered excessive. However, exploratory chromatography had indicated that the benzene-soluble fraction was composed mainly of TNT and that this compound preceded all other components down the column. Consequently, it was felt that loading the columns more heavily than usual would not adversely affect the separation of the more tightly adsorbed substances. This procedure was used to facilitate the location of zones by increasing the amount of adsorbate in each. It was later decided, however, that a preliminary fractionation to remove the TNT would be advantageous if one could be devised.

Attempts to separate the unreacted TNT from the soluble fraction by continuous extractions with n-pentane, n-hexane, n-heptane and carbon tetrachloride were totally unsuccessful. However, using preferential adsorption techniques on short columns of silicic acid-Celite, the benzene-soluble fraction was almost completely freed of its TNT content. Concentrated solutions of the soluble residue in benzene were filtered through columns of adsorbent 5 in. high and 3.5 in. in diameter and the columns washed with benzene until a light brown color approached the bottom. By concentrating the filtrates and repeating the process on fresh columns, the second filtrate was found to contain pure TNT. Using this technique with a solution containing the soluble residue from 250 g of TNT, 188 g of unreacted TNT was recovered. Only an additional 9 g was recovered from this batch in subsequent resolutions.

Attempts to further fractionate the materials left on the column by increasing the displacement power of the solvent were not successful. Although it was from a fraction obtained in this manner that IV was first isolated, generally the procedure produced too many fractions to be practical. In later fractionations the adsorbed materials were eluted from

the columns and treated as single fractions for chromatographic resolution. It will be referred to as the intermediate fraction. Using silicic acid - Celite columns and benzene-*n*-hexane solutions as developers, the intermediate fraction produced chromatograms similar to those described in Figures 1, 2, and 3. However, this adsorbent gave considerably more resolution than silica when used to rechromatograph the initial zones. Particularly was this true with the zones that closely followed TNT on the columns.

It was found that the zone immediately above TNT (zone 2, Figure 3) was composed of 4,6-dinitroanthranil, 2,4,6-trinitrobenzaldehyde, and IV. The order of the quantities of these components present was I > II > IV. Compound IV, which was more difficult to crystallize, could very easily be lost during the crystallization process if the chromatographic resolution was not complete and the compound was not known to be present. Except in one chromatogram which will be described later, IV was never completely separated from I and II chromatographically. The trinitrobenzyl alcohol (V) was found along with VI and VII higher on the column. Considering the probable polar nature of the alcohol, this is as would be expected.

When strongly polar developers such as solutions of methanol in benzene were used on silicic acid-Celite columns, the water was removed from the columns changing the nature of the chromatograms and contaminating the effluent fractions. In order to avoid this, columns of ground silica/e-Celite were used in efforts to resolve the more tightly held zones. Although there was considerable separation and some of the fractions were at least partially crystalline, no additional pure compounds could be isolated.

Continuation of the attempted resolution became increasingly complex and the number of fractions too numerous to be workable. Difficulties stemmed mainly from a lack of knowledge as to when ideal separation had been accomplished and from the inability to cleanly remove zones from the extruded chromatograms. Elution chromatographic techniques were tried in an effort to overcome these difficulties. With the use of this technique, the problem of detection of zones issuing from the column presented itself. This difficulty was overcome through the use of spectrophotometric detection. Previous studies had indicated that many of the components of the decomposition mixture were

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/e G. Frederick Smith silica ground in a ball mill for 4-6 hours and used without screening.

colored and would therefore absorb light in the visible range. Moreover, all of the fractions examined developed colors ranging from red to blue in alkaline solution. It was therefore assumed that a periodic sampling of effluents followed by checks for absorption of alkaline solutions of these samples would serve as a method of zone detection. In order to test this assumption, alkaline ethanolic solutions of TNT, 1,3,5-trinitrobenzene, and six of the compounds isolated from the decomposition mixtures were made. Scans between 700 mμ and 360 mμ were made on a Cary Model 14 recording spectrophotometer at the rate of 0.5 mμ per second. All of the compounds with the exception of VI showed high intensity absorption in this region. Compound VI had a peak of low intensity at 520 mμ, a shoulder at about 420 mμ and an increasing absorption toward the shorter wavelengths. These spectrophotometric results are tabulated in Table 1.

Table II

Spectral Characteristics in Alkaline Solution

Compound	max_1 (mμ)	log	max_2 (mμ)	log	max_3 (mμ)	log
TNT	371	3.9	520	4.1	620[f]	3.8
1,3,5-Trinitrobenzene	427	4.4	500	4.2		
2,4,6-Trinitrobenzaldehyde	426	4.4	507	4.2		
4,6-Dinitroanthranil	498	4.5				
2,4,6-Trinitrobenzyl alcohol	482	4.3				
IV	522-598[h]					
VI	ca. 420[f]		520[g]			
VII	508					

[f] Shoulder. [g] Low intensity peak. [h] Broad plateau

A column of adsorbent 8.5 x 112 cm was used in an attempt to effect the separation of larger quantities of material. Silicic acid - Celite had proved to be the most selective of the adsorbents used but its particle size was such as to require suction for the maintenance of an adequate percolation rate. Columns of silica, on the other hand, had an adequate percolation rate without suction. Since the column could be attended only during the 8-hour workday, and since its size precluded the use of automatic fraction collectors, it was necessary to stop the flow of developers during the overnight periods. This could be done with less complications with gravity flow columns than with those requiring suction. Silica was therefore used in this separation and it was hoped that the added column length would compensate for the lack of selectivity of this adsorbent. An amount of 64 g of the intermediate fraction was adsorbed on the column and development started with benzene-n-hexane 1:1. The strength of the developer was increased stepwise by increasing its benzene content to 2:1, 3:1, 4:1 and then to pure benzene. Further increases in developer strength was achieved by changing to solutions of benzene-chloroform 3:1, 1:1, 1:2 and then to pure chloroform. Following this, a solution of benzene-methanol 2:1 was used and final development was with acetone.

TNT moved down the column first and its movement was detected by long wave length ultraviolet light in which it is visible as a dark band. Its appearance in the effluent was readily detected by the spectrophotometric procedure previously described. An amount of 24 g of TNT was recovered as the initial zone from the column. The second zone yielded 0.44 of solids which proved to be the unidentified compound IV, and was followed by a third zone which contained 1.9 g of almost pure I. Following this was a zone containing 8.9 g of solutes which proved to be a mixture of I and II. (This zone was later resolved by similar techniques on smaller columns of silicic acid, yielding 5.3 g of I and 2.4 g of II.) The fifth zone yielded 0.40 g of nearly pure II. Although this chromatogram yielded IV as a separate zone, its failure to separate I and II caused doubt as to its effectiveness in the separation of the more tightly held components of the mixture.

The continued development of the column gave several additional zones all of which were obviously mixtures. Efforts to crystallize these materials met with little success and at best the products melted over considerable ranges. It was therefore concluded that the adsorbent was not sufficiently selective to separate the more tightly held components.

Although this procedure did not supply a quick and easy method for the separation of the more strongly adsorbed components of the mixture, it offers considerable promise of being developed into an adequate method for this purpose. Its use with a more selective adsorbent, probably silicic acid, and the proper selection of developers may result in the isolation of other pure compounds from the decomposition residue.

EXPERIMENTAL

The major portion of the experimental effort in this research has been expended on the chromatographic resolution of the decomposition residues. Since conditions suitable for such chromatographic work had not been established, much of the effort was of an exploratory nature. To list all of these experiments would require more space than their contribution would warrant. Therefore only enough of the chromatographic work to give a reasonably clear picture of the more successful separations will be described.

General Chromatographic Procedure. Except in separations where special techniques were employed, the following chromatographic procedure was used. Where special techniques were used, the techniques will be described in detail. Unless otherwise specified, the chromatographic tubes used were the tapered type supplied by Scientific Glass Apparatus Company, Bloomfield, New Jersey.

Each tube was fitted with a suction flask of a size sufficient to contain the developer and suction was maintained by a water aspirator. A wad of Pyrex wool was packed in the bottom of the tube, the aspirator was started and the adsorbent was added while the sides of the tube were tapped with a cork ring or other suitable instrument. When sufficient adsorbent had been added to fill the tube to about 85% of its height, the column was firmly tamped and a piece of filter paper was placed on top of the adsorbent column. The top of the column was then prewet with a few milliliters of a suitable solvent. When the meniscus of the wetting solvent had just reached the top of the adsorbent column, the solution containing the mixture to be chromatographed was added. The meniscus of the solution was also allowed to reach the top of the column and the last traces were washed onto the adsorbent with several small portions of developer. The remainder of the developer was introduced through an automatic siphon. During this operation, care was exerted not to allow the top of the adsorbent column to run dry.

After all of the developer had entered the column, suction was maintained for approximately five minutes to remove the excess. The tube was then separated at the joint and the adsorbent column extruded. A fine stream of alcoholic potassium hydroxide was sprayed along the entire length of the column by means of a medicine dropper with a capillary tip. Where zones of poly-nitro aromatic compounds were present, the streak developed bright colors ranging from red to blue. The streak was then scraped off and the zones cut from the column and eluted with a suitable solvent. Solids from the eluates and effluent were recovered by evaporation to dryness in the fume hood.

Decomposition of TNT. In each of ten 9 inch Pyrex test tubes was placed 15 g of Grade 1 TNT which had been recrystallized from acetone and air-dried at room temperature. The tubes were capped with loosely fitting glass stoppers and placed in a vacuum stability block which had been preheated to 200°C. The tops of the tubes protruded from the block approximately 2.5 in. and small amounts of materials which evaporated from the molten mass were condensed in the upper parts of the tubes and on the stoppers. The temperature of the block was maintained at 200°C $\pm$ 1° using a Brown Potentiometer, Model 113CIPS-10, as a controller-recorder. The block was then allowed to cool to approximately 80°C (four to five hours required) and the samples were removed. The decomposition residues were digested in 1500 ml of boiling benzene for 30 minutes, filtered hot and the residue on the filter was washed with 1000 ml of hot benzene. The insoluble residue was 5.0 g/i of a brown powder that did not melt below 360°C. It burned with intumescence leaving an abundance of carbon when ignited in a flame. The solution containing the soluble fraction was concentrated under reduced pressure and used in subsequent chromatography.

Chromatography of Benzene-soluble Fraction on Silica. A solution containing 7 g of the soluble fraction in 75 ml of benzene was chromatographed on a No. 4 column/j of ground silica/e-Celite 5:1. The developer was 800 ml of benzene-ethanol 100:1(vol.). This was repeated until 33 g of the soluble residue had been chromatographed. A representative chromatogram is shown in Figure 1. The zones were eluted with acetone, like zones were combined and the eluates and effluents were evaporated to dryness.

/i The amount of the insoluble residue varied between runs from almost nil to 13% apparently depending upon the accuracy with which the temperature was controlled.

/j No. 4 tubes are 270 mm in length with an average I. D. of 45 mm.

The solids recovered from the combined effluents on evaporation amounted to 30 g. Quantities of materials in zones 1 and 2 were not accurately determined.

The solid material from the preceding effluent fraction was dissolved in 200 ml of benzene and rechromatographed on six No. 4 columns of ground silica-Celite 5:1. The prewetting agent was 40 ml of benzene and the developer was 1500 ml of benzene-methanol 200:1 (vol.). A representative chromatogram is shown in Figure 2. The zones were eluted with acetone, like zones were combined and the effluents and eluates were evaporated to dryness. The combined effluent fractions yielded 28 g of solids. The recovery of solids from zones 1 to 4 amounted to approximately 2 g, nearly equally distributed between the zones. By twice rechromatographing zone 1 using similar procedures, and recrystallizing several times from dioxane-ether, less than 20mg of a straw colored crystalline compound (III), m.p. 217-8°C, was obtained. Anal. - Found: C, 42.10; H, 3.11; N, 23.18. The identity of III has not been established but the analysis indicates that it may be a reduction product of TNT. Attempts to resolve the components of zones 2 to 4 have not been successful.

The solids from the preceding effluent fraction were dissolved in 200 ml of benzene and rechromatographed on five No. 4 columns of ground silica-Celite 5:1. Each column was prewet with 40 ml of benzene and developed with 600 ml of the same solvent. A representative chromatogram is shown in Figure 3. The zones were eluted with acetone, like zones were combined and the eluates and effluents were evaporated to dryness. Zone 1 and the effluent fraction both of which contained only TNT, m.p. 80-81°C, were combined. The total yield was 24 g. The solids recovered from zone 2 weighed 2.4 g, but the weight of the small amount of material from zone 3 was not determined. Zone 2 was crystallized from benzene-n-hexane. The product was apparently a mixture of two types of crystals which melted over the range 98-119°C. It was rechromatographed twice using the above procedure. However, each chromatogram contained one primary zone near the center of the column and the melting point of the crystalline product did not change appreciably. By fractionally crystallizing from benzene-n-hexane, small quantities of I and II were isolated. Compound I formed yellow equants, m.p. 125-6°C. Its elemental analysis gave the empirical formula $C_7H_3N_3O_5$, and suggested that it might be 4,6-dinitroanthranil. When mixed with an authentic sample of this compound prepared by the method of Splitter and Calvin (15), the melting point was not depressed.

Moreover, both I and the authentic sample imparted a red stain to most surfaces with which they came in contact. Anal. Calc. for $C_7H_3N_3O_5$: C, 40.2; H, 1.45; N, 20.1. Found: C, 40.4, 40.0, 40.1, 39.9; H, 1.86, 2.10, 1.77, 1.75; N, 21.0, 20.8. Mol. wt.- Calc. for $C_7H_3N_3O_5$: 209. Found (X-ray): 204. Compound II formed white plates, m.p. 118-119°C, and the melting point was not depressed when mixed with an authentic sample of 2,4,6-trinitrobenzaldehyde. Anal.- Calc. for $C_7H_3N_3O_7$: C, 34.8; H, 1.24; N, 17.4. Found: C, 35.1, 35.0; H, 1.42, 1.39; N, 17.6, 17.5.

Exploratory chromatography of mixtures of I and II on silicic acid using benzene-*n*-hexane solutions as developers showed that the two compounds could be separated chromatographically on this adsorbent.

Preliminary Fractionation of Benzene-soluble Fraction. A solution of the soluble residue from 250 g of TNT in 1250 ml of benzene was fractionated on five columns of ground silica-Celite 5:1. Each column was prewet with benzene and a 250 ml aliquot of the solution was introduced. The column was then washed with 1600 ml of benzene, 1200 ml of benzene-methanol 9:1 (vol.), 1500 ml of benzene-methanol 1:1 (vol.) and finally with 1000 ml of acetone. The effluent from each solvent was taken as a separate fraction. The solids in each fraction were recovered by evaporation of the solvent under reduced pressure. Fractions 1 to 4 yielded 188 g, 17g, 14 g, and 7 g of solids, respectively. Fraction 1 was nearly pure TNT, m.p. 78-81°C, and the chromatography of fractions 2 and 3 is described in the next section. Fraction 4 was added to 18 g of benzene-insoluble material isolated after digestion of the decomposition residue in benzene.

Chromatography of Intermediate Fraction. Fraction 2 from the preliminary fractionation was chromatographed on eight No. 4 columns of silicic acid-Celite 5:1. Approximately 2.1 g quantities of the residue were dissolved in 30 ml of chloroform and introduced onto the columns after prewetting with 50 ml of *n*-hexane. The columns were developed with 900 ml of *n*-hexane-benzene 3:1 (vol.). A representative chromatogram is shown in Figure 4. Both zones were visible without streaking, however the columns were streaked as usual to more clearly define the zoning. An additional 8.8 g of TNT was recovered from the combined effluents. Zones 1 and 2 were eluted with benzene-methanol 20:1 (vol.) and on evaporation of the solvent yielded approximately equal quantities of solids. The amounts were not accurately determined.

By rechromatographing zone 1 using similar procedures, 2.5 g of I were recovered along with traces of TNT. Zone 2 on similar treatment yielded 1.1 g of II and 200 mg of a compound, IV, which formed very fine tan needles, when crystallized from benzene-n-hexane, m.p. 225-7°C. Anal.-Found: C, 42.4, 42.3; H, 2.10, 1.95; N, 21.8, 22.1. The identity of this compound has not been established, but the elemental analysis indicates that it may be a reduction production of TNT.

Fraction 3 from the preliminary fractionation was dissolved in 30 ml of dioxane and the solution diluted with 130 ml of benzene. It was then chromatographed on two No. 6 columns /k of ground silica-Celite 5:1. Each column was prewet with 100 ml of benzene, 80 ml of the solution introduced and the column was developed with 2200 ml of benzene-methanol 200:1 (vol.), 4800 ml of benzene-methanol 100:1 (vol.) and 4000 ml of benzene-methanol 75:1 (vol.). The resulting chromatogram is shown in Figure 5. The zones were visible without streaking. The chromatograms were cut into zones as indicated and eluted with acetone. On evaporating to dryness in the fume hood, the recovery of materials was as follows: effluent, 2.1 g; zone 1, 3.6 g; zone 2, 7.0 g.

The effluent was rechromatographed on silicic acid-Celite 5:1 using benzene-n-hexane solutions as developers. This resulted in the isolation of 1.4 g of I, 0.3 g of II and 0.10 g of a compound, VI, which formed white prisms from benzene-n-hexane, m.p. 132-3°C. Anal.-Found: C, 35.3, 36.0; H, 1.09, 1.18; N, 16.4. The identity of this compound has not been established. Several attempts to isolate pure compounds from zone 1 were unsuccessful. Zone 2 was rechromatographed on silicic acid-Celite 5:1 using benzene-n-hexane solutions as developers. This resulted in the isolation of 330 mg of a compound, V, m.p. 102-3°C, and 0.32 g of a compound, VII, m.p. 221-2°C, which crystallized as fine straw colored needles from benzene-n-hexane. Anal.-Found: C, 41.9, 41.6; H, 1.78, 2.44; N, 22.8, 22.7. The identity of this product has not been established but the analysis indicates that it may be a reduction product of TNT. Compound VI was identified as 2,4,6-trinitrobenzyl alcohol by mixed melting point with an authentic sample. Anal.-Calc. for $C_7H_5N_3O_7$: C, 34.5; H, 2.06; N, 17.6. Found: C, 35.4, 34.5; H, 2.73, 2.69; N, 17.0, 17.2.

/k No. 6 tubes are 330 mm in length with an average I.D. of 70 mm.

Fraction Elution Chromatography. A chromatographic tube 8.5 x 133 cm was fabricated by sealing a length of Pyrex tubing to a coarse sintered glass funnel. The stem of the funnel was fitted with a Teflon stopcock so that the flow of developer could be started and stopped at will. A wad of Pyrex wool was placed in the bottom of the tube and the tube was filled with silica, 50 - 200 mesh, as a slurry in benzene to a height of 120 cm. The column was then charged with a solution of 64 g of the intermediate fraction from the decomposition in 500 ml of benzene. The chromatogram was first developed with benzene-*n*-hexane 2:1 (vol.). The TNT zone appeared slightly darker than the unoccupied adsorbent below it and its movement on the column could be followed. The presence of TNT and subsequent materials in the effluent were detected spectrophotometrically. The materials were recovered by evaporation of the solvents in the fume hood. TNT appeared in the effluent when 20 l of developer had entered the column and its concentration reached a maximum when 34 l had been added. After 42 l of the initial developer had entered the column, the concentration of TNT in the effluent was very low and the developer was changed to benzene-*n*-hexane 3:1 (vol.). The total recovery of TNT was 24 g. When 14 l of the second developer had entered the column, IV appeared in the effluent. An additional 6 l of this developer was added during which time 0.44 g of IV had been isolated. The column was then developed with 36 l of benzene-*n*-hexane 4:1 (vol.) and 38 l of benzene. During the addition of these developers, 1.9 g of I, 8.9 g of a mixture of I and II, and 0.44 g of II were recovered in order. Compound I appeared in the effluent after about 2 l of benzene-*n*-hexane 4:1 (vol.) had been introduced and II had left the column after about 20 l of benzene had been added. Gradually increasing the displacement strength of the developers using benzene-chloroform, chloroform, benzene-methanol, and finally acetone gave numerous zones all of which were mixtures from which no pure compounds could be crystallized. The 8.9 g mixture of I and II was rechromatographed on two No. 4 columns of silicic acid-Celite 5:1, using benzene-*n*-hexane solutions as developers. Products recovered were 5.3 g of I and 2.4 g of II.

Spectrophotometric Detection of Zones. This procedure was developed to detect zones in the effluents of the chromatograms as the effluents issued from the columns. It eliminated the necessity of evaporating fractions to dryness before their contents could be examined, and greatly enhances the selection of fractions. A volume of 1 ml of the effluent was added to ca. 40 ml of ethanol, 3 ml of 0.1N aqueous sodium hydroxide was

added and the solution was diluted to 50 ml with ethanol. The spectrum between 700 and 360 mμ was run on a Cary Model 14 recording spectrophotometer at the scanning rate of ten angstroms per second. By use of a Cary Model 1015 program attachment, the operation of the spectrophotometer was made automatic. The appearance of polynitro aromatic compounds in the effluents was detected by the appearance of characteristic absorption. Changes in the concentrations of solutes were indicated by changes in the optical densities of the effluents. Variations in the optical densities without variations in the shape of the curve usually indicated that a pure compound was issuing from the column. Gradual changes in the shape of the curve indicated that the effluent contained a mixture and that the relative concentrations of the components varied as the development progressed. Compounds whose absorption characteristics were known were identified as they issued from the column. The frequency of scans depended upon the size of the column, the rate of percolation and the absorption of the effluent fractions. When the effluents showed no absorption, spectral examinations were less frequent than when a zone was in the process of leaving the column.

<u>Proof of the Absence of 1,3,5-Trinitrobenzene among the Decomposition Products</u>. Exploratory chromatography of mixtures of 1,3,5-trinitrobenzene, TNT and 4,6-dinitroanthranil (I) on silicic acid-Celite columns showed that 1,3,5-trinitrobenzene was adsorbed on the columns between TNT and I.

A solution containing 50 mg each of 1,3,5-trinitrobenzene and I, and 30 mg of TNT in 15 ml of benzene was adsorbed on a No. 2/1 column of silicic acid-Celite 5:1 and developed with 350 ml of <u>n</u>-hexane-benzene 5:2 (vol.). The column of adsorbent was extruded and streaked with alcoholic sodium hydroxide. Three distinct zones appeared on the chromatogram even though the lead zone was only slightly below the center of the column. The zones were eluted with benzene-methanol 20:1 (vol.) and their contents identified by melting point. In order from bottom to top, the zones contained TNT, 1,3,5-trinitrobenzene and I. Similar techniques on decomposition fractions known to contain compounds in the chromatographic region of TNT to 2,4,6-trinitrobenzaldehyde did not show the presence of 1,3,5-trinitrobenzene.

/1 No. 2 tubes are 200 mm long and 19 mm in diameter.

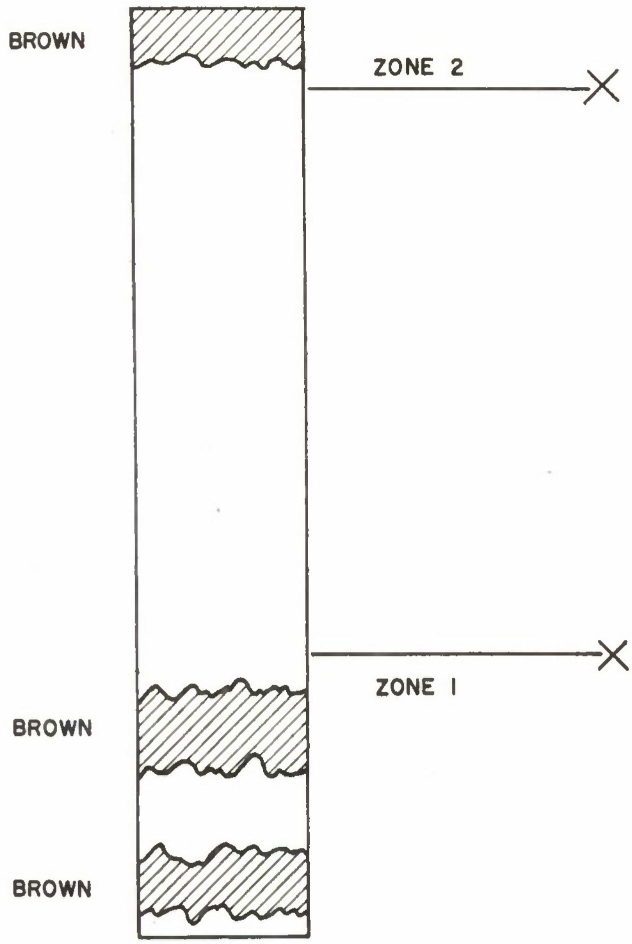

FIG. 1 CHROMATOGRAM OF 7 G OF BENZENE—SOLUBLE FRACTION ON NO. 4 COLUMN OF GROUND SILICA-CELITE 5:1 DEVELOPED WITH 800 ML OF BENZENE-ETHANOL 100:1 (VOL.) COLORS SHOWN WERE VISIBLE WITHOUT STREAKING

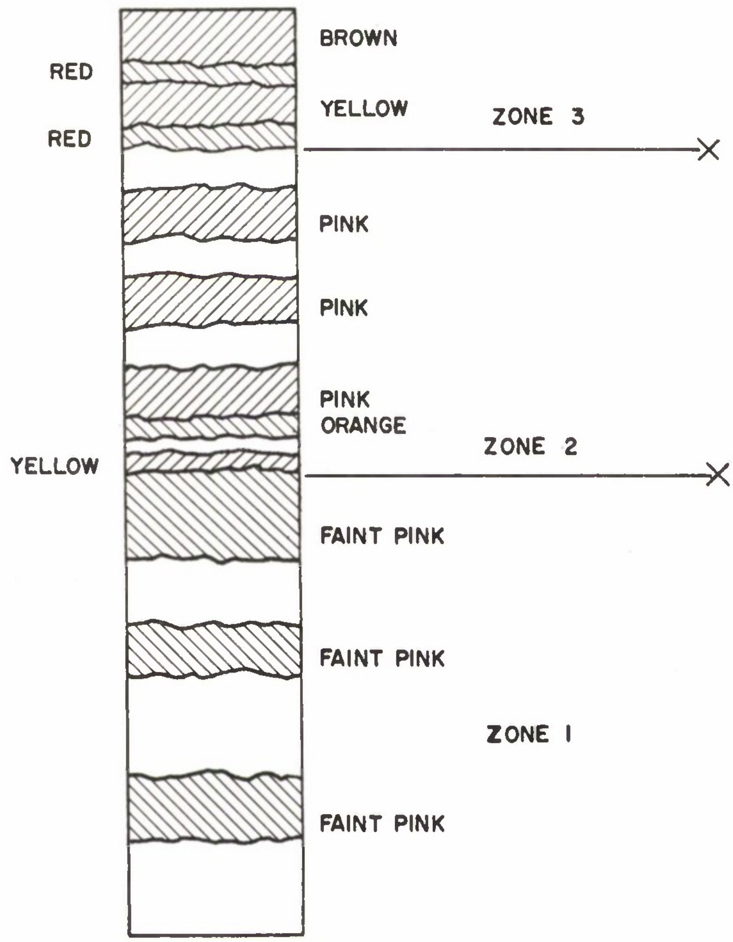

FIG. 2 CHROMATOGRAM OF 5 G OF THE EFFLUENT FRACTION, FIGURE 1, ON NO. 4 COLUMN OF GROUND SILICA-CELITE 5:1 DEVELOPED WITH 1500 ML OF BENZENE-METHANOL 200:1 (VOL.)

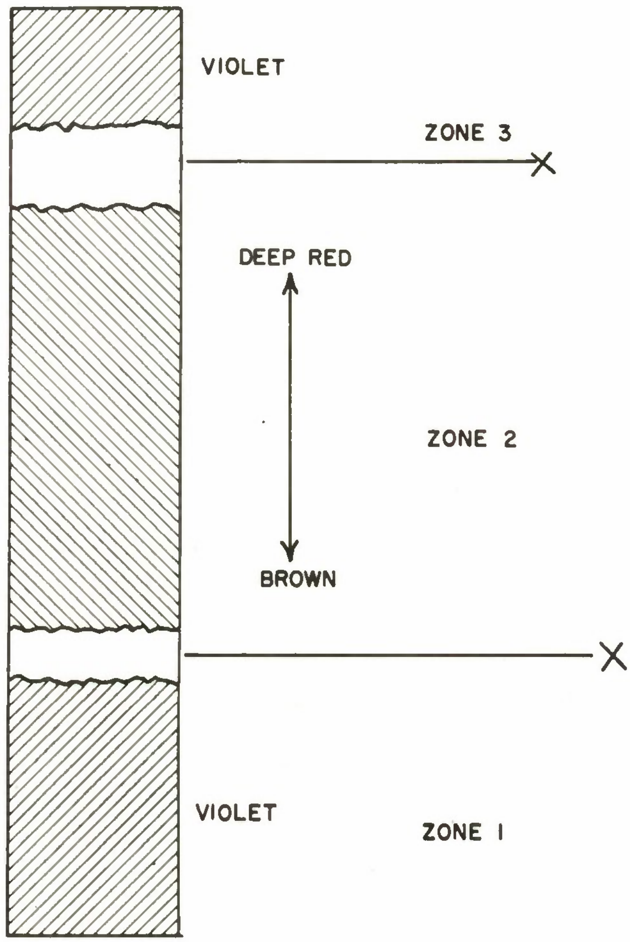

FIG. 3 CHROMATOGRAM OF 5.6 G OF THE EFFLUENT FRACTION, FIGURE 2, ON NO. 4 COLUMN OF GROUND SILICA-CELITE 5:1 DEVELOPED WITH 600 ML OF BENZENE.

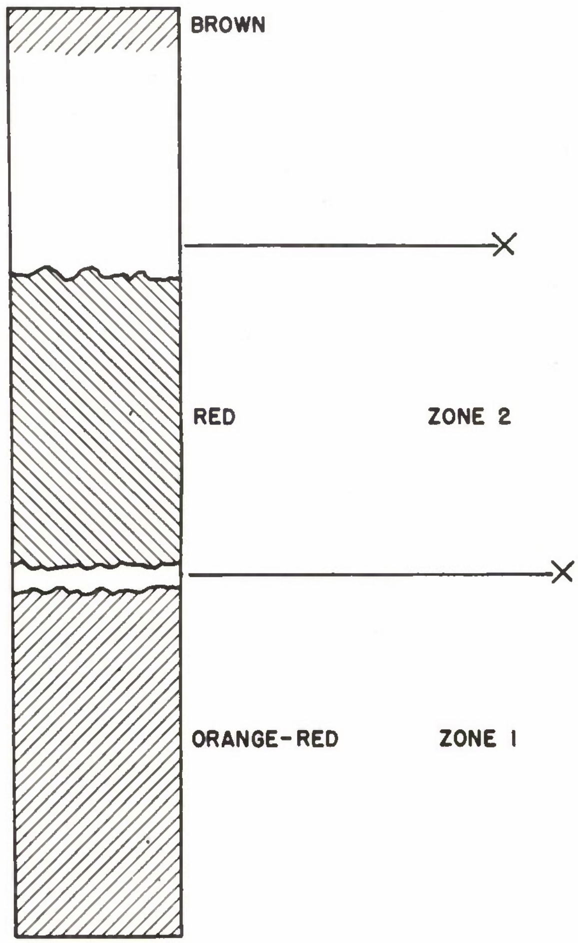

FIG. 4 CHROMATOGRAM OF 2.1 G OF FRACTION 2, PRELIMINARY FRACTIONATION ON A NO. 4 COLUMN OF SILICIC ACID-CELITE 5:1 DEVELOPED WITH 900 ML OF HEXANE-BENZENE 3:1 (VOL.)

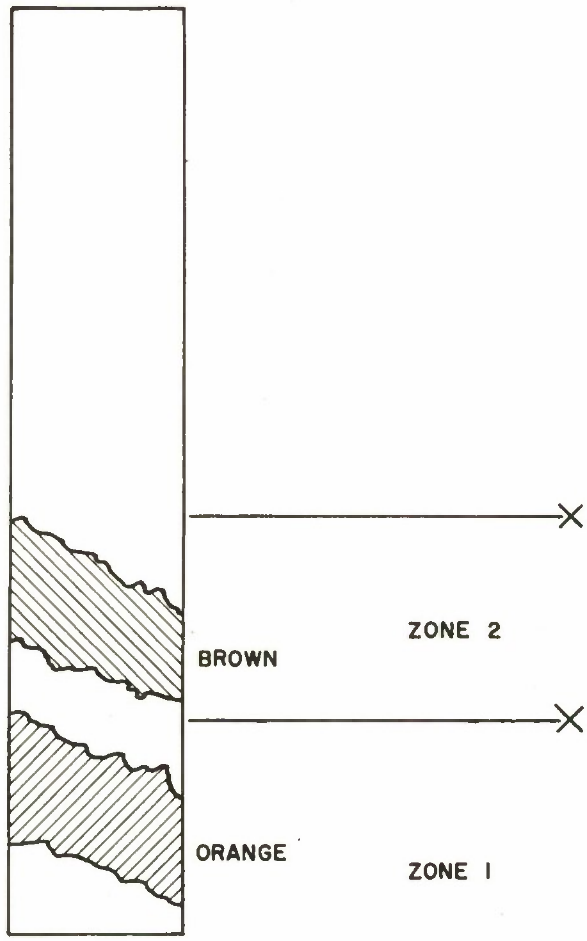

FIG. 5 CHROMATOGRAM OF 7 G OF FRACTION 3, PRELIMINARY FRACTIONATION, ON NO. 6 COLUMN OF GROUND SILICA-CELITE 5:1 DEVELOPED WITH 2200 ML BENZENE-METHANOL 200:1 (VOL.), 4800 ML BENZENE-METHANOL 100:1 (VOL.) AND 4000 ML BENZENE-METHANOL 75:1 (VOL.). COLORS SHOWN WERE VISIBLE WITHOUT STREAKING.

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